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(54) RESIN IMPREGNATED LAMINATE FOR WIRING BOARD APPLICATIONS

HARZIMPRAEGNIERTES LAMINAT ZUR ANWENDUNG IN LEITERPLATTEN

STRATIFIE IMPREGNE DE RESINE POUR LA REALISATION DE CARTES A CIRCUITS IMPRIMES

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- DATABASE WPI Week 7951, Derwent Publications Ltd., London, GB; AN 79-92216 ANONYMOUS 'Mixed aramid paper prepd. from floc and fibre particles'
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Description

BACKGROUND OF THE INVENTION

To provide consumers with increasing functionality at lowest possible cost the electronics industry is driving towards products which are smarter, faster and smaller. This evolution is being promoted by advances in semiconductor materials and fabrication technology, such as multilayer IC (integrated circuits), submicron IC features and large scale integration. Packaging and interconnect technologies play a key supporting role in the evolution. Materials for packaging and interconnect technologies must support high yield fabrication, high density packaging, fast signal propagation and compatibility with surface mount and direct attach of components. To meet these requirements reinforcements with lower in-plane CTE (coefficient of expansion), greater dimensional stability, lower dielectric constant and smooth surfaces are needed.

CTE is an important property for the printed wiring board (PWB) substrate especially in the surface mount and direct attach chip applications. CTE mismatch between the chip (or chip carrier) and the board pose reliability problems due to potential solder joint cracking during thermal cycling. Various techniques were developed to insure some reliability of the solder joints, e.g., "J" leads, gull wing leads, leaded chip carriers and leadless chip carriers. However, the high (13-18 ppm/°C) in-plane CTE of the standard epoxy/E-glass or polyimide/E-glass still resulted in some solder joint failures. In order for components to successfully survive environmental testing, in-plane CTE's of 8-10 ppm/°C are necessary.

The successful production of multilayer PWBs also requires layer-to-layer pad registration and registration of through holes to pads. During fabrication of PWBs, laminate materials experience a number of thermal excursions, including bake cycles at 120-150°C and short exposures to temperatures as high as 280°C. In general, these thermal exposures cause dimensional change in the laminate materials.

Normally, and especially in the case of p-aramid fibers, the fiber CTE is much lower than the resin CTE. It is possible to make low CTE laminates using very low resin contents (<40 wt%), where the fiber properties dominate the composite properties such as described in USA 4,729,921 which teaches control of CTE by lowering resin content.

In these known laminates, the nonwoven aramid reinforcement sheet can comprise paramid floc and poly(m-phenylene isophthalamide) fibrids as a binder, in an amount of 5 to 25 % by weight, of the total solids. However, this laminate would have low peel strength, voids, etc. and would not meet all the property requirements for a reliable PWB, and is not a practical route to make PWBs.

Summary of the Invention

The present invention provides a nonwoven aramid sheet useful as reinforcement in printed wiring board laminates, said nonwoven aramid sheet having a coefficient of thermal expansion of less than 10 ppm per °C, said sheet comprised of from 5 to 25 weight percent poly(m-phenyleneisophthalamide) fibrids and 75 to 95 weight percent p-aramid floc, and the dried sheet having a basis weight of between 27 and 136 g/m^2 (0.8 and 4.0 oz/yd^2), a density between 0.5 and 1.0 g/cm^3 and a Gurley Hill Porosity of less than 10 sec.

Also provided is a thermoset resin laminate of high dimensional stability suitable for printed wiring board substrate consisting essentially of thermoset resin reinforced with from 43 to 57 weight percent of the nonwoven aramid sheet of this invention.

Detailed Description of the Invention

The reinforcement of the laminates of this invention is a nonwoven aramid sheet having a coefficient of thermal expansion (CTE) of less than 10 ppm per °C and is prepared from 75 to 95 wt.% p-aramid floc and from 5 to 25 wt.% poly(m-phenylene isophthalamide) fibrids. Floc is defined in U.S. Patent No. 4,729,921 as staple fibers having a length of 12.7mm (0.5 inches) or shorter. Paraaramid fibers are very high in strength and modulus. Examples of para-aramids are set out in U.S. Pat. No. 3,869,429 and in European Patent 330,163. Specific examples of para-aramids are poly (p-phenylene terephthalamide) (PPD-T) and copoly(p-phenylene-3,4'-oxydiphenylene terephthalamide). Fibers of PPD-T are generally made by an air gap spinning process such as described in U.S. Pat. No. 3,767,756; are preferably heat treated as described in U.S. Pat. No. 3,869,430. Preferably poly(p-phenylene terephthalamide) floc which has not been refined, i.e., as prepared, is employed. High shear forces exerted on the fibers during processing, e.g., refining, causes damage to the fibers and adversely affect the CTE of the reinforcement. It is also preferred to employ p-aramid floc of high orientation and relatively lower crystallinity. Fibrids are defined in U.S. 4,729,921 as small non-granular, non-rigid fibrous or film-like particles. Two of their three dimensions are on the order of microns. Aromatic polyamide fibrids may be prepared by precipitating a solution of the aromatic polyamide into a coagulating liquid as for example using fibridating apparatus of the type disclosed in U.S. Patent No. 3,018,091.

To prepare the sheet, the floc and fibrids are dispersed in the desired proportions as an aqueous slurry, the solids concentration generally ranging between 0.005% and 0.02%. The slurry is not refined. The slurry can be made into paper by conventional means. In the examples which follow, wet sheets were formed in an inclined wire Deltaformer (papermaking machine) and dried using heated drier cans. The dried sheets preferably having a basis weight between 27 and 136 g/m^2 (0.8 and 4.0 oz/yd^2), are then calendered between two hard-surface rolls. Calender pressures between about 500 and 2500 kg/cm (nip pressure) and roll temperatures between about 130°C and 150°C are commonly employed. The density of the paper reinforcement is between 0.5 and 1.0 g/cm^3 the paper should has a Gurley Hill Porosity of less than 10 sec.

The paper is then prepregged with a resin having a high Tg, e.g., above about 160°C. In the examples that follow, the papers were impregnated on a vertical prepegging tower using an epoxy resin system, Tg about 170°C.

The CTE of the reinforced composite is a function of the sheet as well as the resin. The CTE of the p-aramid fabric is normally much lower than that of the resin. However, the use of low resin content, while resulting in a low overall CTE, causes other problems. Since there is less resin to act as an adhesive between laminate layers, the peel strength is diminished. Low resin content will also lead to higher void content and greater likelihood of blister formation when the air entrapped in the voids expands upon heating of the PWB.

As mentioned previously it is important that the paper reinforcement have a density of between 0.5 and 1.0, preferably 0.7 to 0.95 g/cm^3 to provide dimensional stability during fabrication of printed wiring boards. Less resin is required to fully saturate a more dense paper, i.e., one that has fewer voids. This results in a better overall CTE since as mentioned previously the CTE of the resin is normally much greater than that of the floc.

The following examples are illustrative of the present invention.

EXAMPLES

An aqueous slurry comprised of about 79 to 89% by weight of floc (short fibers less than 12.7 m (0.5 in.), long) of poly(p-phenylene terephthalamide) and 11 to 21% by weight of refined poly(m-phenylene isophthalamide) fibrids was prepared at a solids concentration of between 0.005 and 0.02%. Proportions of floc and fibrid are reported in Table 1. The slurry was formed into wet sheets as described above and dried. The dried sheets having a basis weight (B.W.) reported in the Table, were calendered at a pressure between 554 and 1676 kg/cm (nip pressure). The papers having a thickness after calendering as reported in Table 1 had a calculated density of between 0.53 and 0.87 g/cm^3 as reported in Table 1.

The paper was prepregged as described above with epoxy resin, the resin content for each item being shown in Table 1. Laminates were prepared by pressing 14 to 16 layers of the prepregs sandwiched between 28g (1 oz) copper foil on each side in a vacuum press using the following press (time/temp) cycle: 1 minute at 93°C (200°F), 0.5516 bar (8 psi); 40 minutes at 177°C (350°F), 41.37 bar (600 psi); 30 minutes at 204°C (400°F), 13.79 bar (200 psi); and 5 minutes at 38°C (100°F), 6.895 bar (100 psi). Specimens were cut from the thick laminates and the copper was etched off. The CTE was measured in the MACHINE-"X", and CROSS-"Y", directions using a DuPont Thermomechanical Analyzer and the results reported in Table 1.

TABLE 1

(1 mil = 25.4	Item 1	Item 2	Item 3	Item 4	Item 5	Item 6	Item 7
Paper Composition	83% floc 17% fibrid	83% floc 17% fibrid	83% floc 17% fibrid	86% floc 14% fibrid	88% floc 11% fibrid	88% floc 12% fibrid	89% floc 11% fibrid
Paper B.W. (oz/yd^2) (1oz/yd^2 = 34.09 g/m^2)	1.69	1.66	1.66	2.07	1.67	1.60	1.61
Paper Thickness (mils) (1 mil = 25.4 µm)	2.6	3.3	2.6	3.3	4.2	3.3	2.5
Gurley Hill Porosity (Sec)	1.8	0.6	0.9	0.9	0.2	26.2	338.0
Paper Density	0.87	0.67	0.85	0.84	0.53	0.65	0.86
Resin Conc. (%)	47.8	2.9	50	52.4	49.1	53.3	48.2
CTE X direction	6.6	6.7	7.6	8.8	6.9	9.0	13.8
Y direction	6.8	8.8	10.6	9.1	8.3	18.3	16.6
X-Y Average	6.7	7.75	9.1	8.95	7.6	13.65	15.2

Claims

1. Nonwoven aramid sheet useful as reinforcement in electronic printed wiring board laminates, said nonwoven aramid sheet having a coefficient of thermal expansion of less than 10 ppm per °C, said sheet comprised of from 5 to 25 weight percent poly(m-phenylene isophthalamide) fibrids and 75 to 95 weight percent p-aramid floc and the dried sheet having a basis weight of between 27 and 136 g/m^2 (0.8 and 4.0 oz/yd^2) and a density between 0.5 and 1.0 g/cm^3 and a Gurley Hill Porosity of less than 10 seconds.

2. A nonwoven aramid sheet according to claim 1 having a density between 0.7 and 0.95 g/cm^3.

3. A nonwoven aramid sheet according to claim 1 wherein the p-aramid floc is poly(p-phenyleneterephthalamide).

4. A thermoset resin laminate of high dimensional stability suitable for printed wiring board substrate consisting essentially of thermoset resin reinforced with from 43 to 57 weight percent of the nonwoven aramid sheet of claim 1 or 2.

Patentansprüche

1. Nonwovenaramidflächengebilde, das als Verstärkung in Laminatplatten für elektronische gedruckte Schaltungen geeignet ist, wobei das Nonwovenaramidflächengebilde einen Wärmeausdehnungskoeffizienten von weniger als 10 ppm pro °C besitzt, das Flächengebilde aus 5 bis 25 Gew.-% Poly(m-phenylenisophthalamid)fibriden und 75 bis 95 Gew.-% p-Aramidflocke besteht, und das getrocknete Flächengebilde ein Flächengewicht von zwischen 27 und 136 g/m^2 (0,8 und 4,0 Unzen/$Yard^2$) und eine Dichte zwischen 0,5 und 1,0 g/cm^3 und eine Gurley-Hill-Porosität von weniger als 10 Sekunden hat.

2. Ein Nonwovenaramidflächengebilde gemäß Anspruch 1 mit einer Dichte zwischen 0,7 und 0,95 g/cm^3.

3. Ein Nonwovenaramidflächengebilde gemäß Anspruch 1, worin die p-Aramidflocke Poly(p-phenylenterephthalamid) ist.

4. Ein als Substratplatte für gedruckte Schaltungen geeignetes Laminat mit hoher Dimensionsstabilität aus hitzegehärtetem Harz, das im wesentlichen aus hitzegehärtetem Harz besteht, das mit 43 bis 57 Gew.-% des Nonwovenaramidflächengebildes nach Anspruch 1 oder 2 verstärkt ist.

Revendications

1. Feuille d'aramide non-tissée utile en tant que renfort dans des stratifiés de cartes de circuits imprimés électroniques, ladite feuille d'aramide non-tissée ayant un coefficient de dilatation thermique inférieur à 10 ppm par °C. ladite feuille comprenant de 5 à 25 % en poids de fibrides de poly(m-phénylène isophtalamide) et de 75 à 95 % en poids de flocs de p-aramide, et la feuille séchée ayant un grammage compris entre 27 et 136 g/m^2 (entre 0,8 et 4,0 oz/yd^2) et une masse spécifique comprise entre 0,5 et 1,0 g/cm^3, ainsi qu'une porosité Gurley Hill inférieure à 10 secondes.

2. Une feuille d'aramide non-tissée selon la revendication 1, ayant une masse spécifique comprise entre 0,7 et 0,95 g/cm^3.

3. Une feuille d'aramide non-tissée selon la revendication 1, dans laquelle les flocs de p-aramide sont en poly(p-phénylène téréphtalamide).

4. Un stratifié de résine thermodurcissable ayant une grande stabilité dimensionnelle, convenant à un substrat de carte de circuits imprimés, constituée essentiellement d'une résine thermodurcissable renforcée par 43 à 57 % en poids de la feuille d'aramide non-tissée de la revendication 1 ou 2.